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Optimizing Hercosett/Optical Brightener Agent/Hydrogen Peroxide Systems Applied to Untreated Wool for Shrinkproofing

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ABSTRACT

We have studied the application on untreated wool fibers of different aqueous dispersion systems made with Hercosett, a cationic resin; three commercial anionic optical brightener agents (OBA), Uvitex CF-200, Blankophor BA Liq. B, and Uvitex NFW; and the oxidative agent hydrogen peroxide to improve both whiteness and shrinkproofing properties with less damage to the keratinic structure. Treatment times and temperatures were optimized using the central composite rotatable design of Box and Hunter and, in all cases, a weight ratio of Hercosett/OBA that produced better shrinkproofing. Results obtained for each OBA were also compared to determine optimum application.

Many chemical compounds have been described in the literature as fluorescents, and in the last 40 years intensive research has yielded many more fluorescent compounds suitable for whitening [1, 9, 19]. Optical brightener agents (OBA) absorb the ultraviolet portion of the daylight spectrum invisible to the eye and convert the energy thus taken up into the longer-wavelength visible portion of the spectrum, *i.e.*, blue-violet light.

Hercosett resin is a reactive cationic crosslinked polymer [10, 11] capable of forming insoluble aggregates in aqueous media in the presence of anionic surfactants, provided the amount of surfactant is maintained within certain limits [5, 6]. Previously, we investigated the use of anionic surfactants in applying Hercosett resin to untreated wool fabrics to impart shrinkproofing properties [7].

A mixture of Hercosett resin and different anionic optical brightener agents (OBA) in an aqueous medium may form insoluble aggregates, depending on the ratio of the two species [14]. Insoluble aggregates are formed by ionic interaction between the two components, and when the brightener concentration is increased, the aggregates become soluble. Hydrophobic linkages are thus also implicated [3].

In an earlier paper, we described a process to minimize the shrinkage of wool fibers based on the formation of a complex of Hercosett resin, the anionic optical brightener agent Uvitex NFW, and hydrogen peroxide as the oxidative agent, and its interaction with untreated wool fibers. In this way, in addition to providing satisfactory shrinkproofing, brightness characteristics could be substantially improved. Likewise, we studied degradative effects caused by these systems on knitted wool fabrics and optimized the results [4].

In this work, we have compared the results of applying different dispersion systems on untreated wool fibers: Hercosett resin, hydrogen peroxide, and three commercial anionic optical brightener agents, Uvitex CF-200, Blankophor BA Liq. B, and Uvitex NFW. Time and temperature parameters have been optimized for each OBA in the range between 5 and 20 minutes and 35C and 80°C, using in all cases a weight ratio of both OBA and resin components that promotes better shrinkproofing properties.

Experimental

The wool sample was a fabric knitted to a cover factor of 1.2 from R72-tex/2 botany wool yarns. Hercosett 57, which is a polyamide-epichlorhydrin resin in a 10% active aqueous solution, was manufactured by Hercules Chemical Co. Optical brightener agents were Blankophor BA Liq. B (stilbenedisulphonic acid derivative), CI fluorescent brightener 113 manufactured by Bayer S.A., Uvitex CF-200 (stilbenesulphonic acid derivative), CI fluorescent brightener 134, and Uvitex NFW (distearylbiphenyl derivative) from Ciba-Geigy S.A. The oxidative agent (hydrogen peroxide) was a 30% (w/v) aqueous solution (Probus S.A.)

Shrinkage of wool fabrics was tested at a liquor ratio of 30:1 and a 1 kg load for 3 hours at 40°C; the pH was held at 7.5 by a phosphate buffer according to the superwash test in a Cubex apparatus [15].

Cysteic acid and alkaline solubilities of the treated wool fabrics were determined in accordance with the methods of the International Wool Textile Organization [17, 18]. The ball penetration resistance loss (expressed as BPR in percent) of treated samples was evaluated with a pendulum instrument [13]. The whiteness index of the treated samples was estimated by an Elrepho photometer, using the tristimulus colorimetry technique [8]. A 100% whiteness index was defined as the level of whiteness obtained for samples treated with OBA using treatment conditions recommended by the manufacturer.

Dispersion systems consisting of Hercosett resin/OBA/hydrogen peroxide were prepared by progressively adding increasing amounts of each OBA aqueous solution to the solution containing Hercosett (2 grams of dry solid basis/liter) and a 2 volume concentration of hydrogen peroxide with vigorous stirring at 20°C in a glass container. The pH value of the systems was buffered with a phosphate buffer and adjusted to 7.0.

Untreated wool samples (10 g) were then immersed in these aqueous ternary dispersion systems and treated for 20 minutes at 20°C with occasional stirring at a bath ratio of 1:30 and pH of 7.0. After treatments, the samples were extracted to approximately 80% pickup and then dried and cured in a forced air oven at 80°C for 60 minutes.

Results and Discussion

OBA/HERCOSETT/HYDROGEN PEROXIDE SYSTEMS

Figure 1 shows the shrinkage area percent of the knitted wool samples treated with ternary systems freshly prepared with Hercosett (2 g/l), hydrogen peroxide (2 volume), and increasing amounts of Uvitex NFW, Uvitex CF-200, and Blankophor BA Liq. B (ranging from 0.1 to 6 grams of OBA per gram of Hercosett resin). Amounts of the OBA from 1.5 to 3.5 g/g of Hercosett resin enhance shrinkage properties in untreated wool, attaining values less than 10%, the maximum acceptable in accordance with the superwash test of the Wool Foundation [15]. Amounts of OBA exceeding 4 g/g of Hercosett resin produce dispersions with smaller optical density values, which do not enhance shrinkproofing properties when applied to untreated wool, especially the Hercosett/Uvitex NFW system.

STATISTICAL TREATMENTS OF RESULTS

Since the hydrogen peroxide reagent exerts an oxidizing influence on the keratinic structure of wool fibers, we studied some physicochemical parameters of treated wool that provide a suitable measure of its oxidation level, including shrinkproofing values, whiteness index, ball penetration resistance loss, cysteic acid content, and alkaline solubility. We used the central composite rotatable design of Box and Hunter [2] for two variables, time (X_1) and temperature (X_2), the experimental levels of which are shown in Table I. The following parameters were constant: Hercosett resin concentration (2 g/l), hydrogen peroxide concentration (2 volume), OBA concentration (2 g/g Hercosett resin), bath ratio (1:30). The results are shown in Table II, and Table III gives the regression coefficients in codified variables, as well as the significance of the regression coefficients and the lack of fit obtained in the variance analysis.

Bearing in mind that the lack of fit is not significant in any of the parameters given in Table III, the response surfaces satisfactorily represent the properties studied as a function of treatment time and temperature. In addition, the first or second-degree terms of the adjusted equations are significant at the 1, 5, or 10% level, except for the shrinkage area percent in the presence of Blankophor. However, considering that both *F*-Shedecor values obtained in the regression analysis of variance test (ANOVA) [12] for the first and second-degree terms have a significance level near 10%, we can state that the adjusted surface also adequately represents this phenomenon. The larger dispersion occurring in the five central replicates could explain this lower significance level for the shrinkage area percent for the Blankophor/Hercosett system.

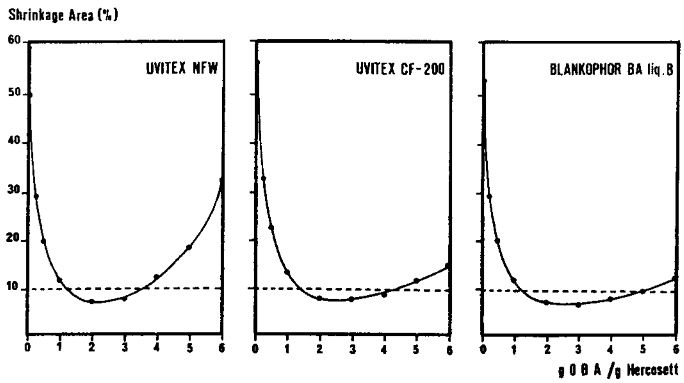

FIGURE 1. Shrinkage area percent of wool samples treated with OBA/Hercosett/H_2O_2 complexes versus OBA/Hercosett ratio.

TABLE I. Variables of the central composite rotatable design of Box and Hunter for the application of Hercosett/optical brightener agents/hydrogen peroxide aqueous systems on untreated wool samples and experimental levels of treatment in these variables.

	Codified levels				
Variables	−1.414	−1	0	1	1.414
X_1 = treatment time	1 min	3 min 45 s	10 min 30 s	17 min 15 s	20 min
X_2 = treatment temperature, °C	20	28.8	50	71.2	80

TABLE II. Results of the parameters in the central composite rotatable design of Box and Hunter for the variables of time ($X1$) an temperature ($X2$) for application of Hercosett/OBA/hydrogen peroxide aqueous systems on untreated knitted wool samples.[a]

	Values of variables		BPR, %			Alkaline solubility, %			Shrinkage area, %			Whiteness index, %			Cysteic acid, %		
Treatment	X_1	X_2	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
1	−1	−1	1.0	1.7	1.8	18.2	19.0	18.5	15.4	12.8	15.0	46	47.7	48	0.57	0.59	0.54
2	1	−1	4.6	5.7	7.0	19.8	20.5	20.0	16.0	12.0	14.0	46	45.6	46	0.78	0.80	0.80
3	−1	1	4.6	5.7	7.0	19.5	20.4	19.5	19.2	15.6	14.8	98	99.8	97	0.81	0.84	0.80
4	1	1	10.0	9.7	12.0	24.8	25.4	24.5	9.5	7.6	17.0	110	108.0	108	1.29	1.32	1.35
5	−1.414	0	2.6	2.7	3.3	16.2	17.2	16.2	17.8	15.6	8.0	70	68.0	67	0.80	0.80	0.85
6	1.414	0	8.0	8.5	10.8	22.0	22.0	21.5	11.5	9.2	17.0	75	73.0	75	0.91	0.96	0.97
7	0	−1.414	2.6	2.8	3.3	19.7	20.1	19.5	14.5	12.0	10.0	40	38.0	39	0.54	0.59	0.54
8	0	1.414	8.0	8.5	10.5	24.0	24.0	23.5	12.9	10.8	14.0	120	118.0	118	1.10	1.17	1.19
9	0	0	3.8	3.6	5.1	18.0	19.0	18.0	10.0	8.0	13.0	55	50.0	54	0.75	0.76	0.87
10	0	0	3.6	3.8	5.2	21.0	20.0	21.0	8.0	9.0	8.0	58	53.0	55	0.95	0.97	0.69
11	0	0	3.7	3.4	4.9	18.0	18.0	19.0	9.0	7.0	10.0	53	51.0	53	0.84	0.87	0.98
12	0	0	3.2	3.6	4.8	19.0	21.0	17.0	9.0	8.0	8.0	54	52.0	56	0.79	0.79	0.80
13	0	0	3.9	3.7	5.2	20.0	19.0	19.0	8.0	9.0	9.0	55	51.0	54	0.90	0.88	0.80

[a] A = Uvitex CF200, B = Uvitex NFW, C = Blankophor BA.

TABLE III. Regression coefficients in codified variables, significance level of regression coefficients, and lack of fit deviation of the adjustment obtained in the variance analysis.

			Regression coefficients					Significance level		
Parameter	OBA[a]	Independent terms	X_1	X_2	X_1^2	X_2^2	X_1X_2	First-degree terms	Second-degree terms	Lack of fit
BPR, %	A	3.61	2.063	2.045	0.995	1.020	−0.075	1%	1%	NS
	B	3.64	2.079	2.079	0.768	0.768	0.450	1%	1%	NS
	C	5.04	2.601	2.548	0.999	0.924	−0.050	1%	1%	NS
Alkaline solubility, %	A	19.20	1.888	1.548	−0.025	1.350	0.925	5%	NS	NS
	B	19.40	1.661	1.477	0.225	1.450	0.875	5%	NS	NS
	C	18.80	1.749	1.395	0.138	1.463	0.875	10%	NS	NS
Shrinkage area, %	A	8.80	−2.251	−0.620	3.138	2.663	−2.575	1%	1%	NS
	B	8.20	−2.231	−0.412	2.125	1.625	−1.800	5%	5%	NS
	C	9.60	1.941	0.857	2.188	1.938	0.800	NS	NS	NS
Whiteness index, %	A	55.00	2.384	28.640	8.438	12.188	3.000	1%	1%	NS
	B	51.40	1.646	28.453	9.806	13.556	2.575	1%	1%	NS
	C	54.40	2.539	27.838	8.300	12.050	3.250	1%	1%	NS
Cysteic acid, %	A	0.846	0.106	0.193	0.011	−0.007	0.068	5%	NS	NS
	B	0.854	0.115	0.199	0.015	0.015	0.068	1%	NS	NS
	C	0.818	0.122	0.216	0.042	0.020	0.073	5%	NS	NS

[a] A = Uvitex CF200, B = Uvitex NFN, C = Blankophor BA.

To determine the experimental conditions that lead to an acceptable level of both shrinkproofing and whiteness with less physicochemical damage, we present graphically the surface response for each OBA/Hercosett system in a range of times and temperatures that includes the acceptable shrinkage level (lower than

10%) for the three OBA/Hercosett systems considered, that is to say, time values from 5 to 20 minutes and temperature values between 35 and 80°C.

Figure 2 shows these optimal conditions for the Blankophor/Hercosett system obtained in a short time at low temperature, and for Uvitex CF-200/Hercosett and Univex NFW/Hercosett systems in a wider optimal zone (except for a short time range or a long time and low temperature range).

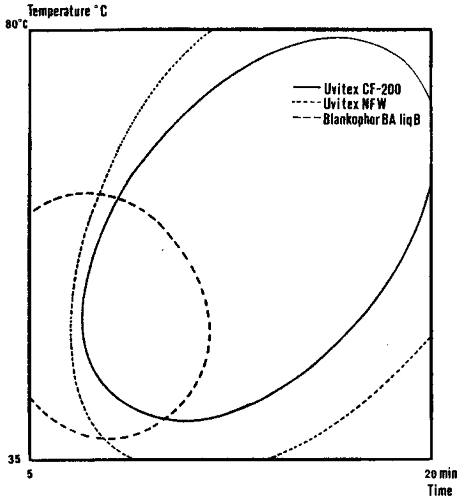

FIGURE 2. Box-Hunter optimization response surface diagram of shrinkage area percent (10%) of wool samples treated with OBA/Hercosett/H_2O_2 versus treatment time and temperature.

During applications of Hercosett/H_2O_2/OBA complexes on untreated wool knitted samples, two phenomena take place simultaneously: first, the attraction and fixation of OBA/Hercosett complexes on wool, which improves physical properties, and second, an oxidative effect due the presence of the oxidizing agent hydrogen peroxide, which promotes the formation of active sites of cysteic acid where OBA/Hercosett complexes can be ionically linked. This also could affect the stability of OBA/Hercosett disperse systems. As a consequence, we present the following discussion of the results in Figures 3–7 in an attempt to establish any relation between OBA/Hercosett disperse systems and any specific improvements.

SHRINKPROOFING PROPERTIES

Figure 3 shows that at short times, the influence of temperature on the shrinkage area percent is the same whatever the OBA/Hercosett system, the Blankophor/Hercosett system yielding the best results. For longer treatments, the shrinkage area percent increases with the Blankophor/Hercosett system but decreases with the two other Uvitex/Hercosett systems, reaching an optimal stable zone. For longer treatments, the Blankophor/Hercosett system shrinkage area increases with temperature, because the influence of temperature on shrinkage is stronger as time increases.

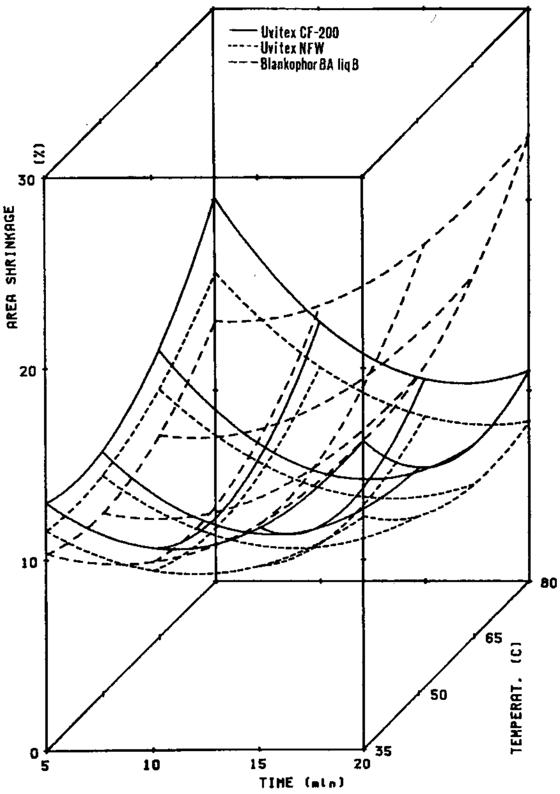

FIGURE 3. Spatial response surfaces of shrinkage area percent of treated wool fabrics with different OBA/Hercosett/H_2O_2 complexes versus time and temperature.

For the two Uvitex/Hercosett systems, the effect of temperature on shrinkage area decreases when time increases, reaching a slight reverse effect. In this case, higher temperatures lead to better shrinkproofing.

The acceptable shrinkage zone (lower than 10%) in the Blankophor/Hercosett system would be bounded for time values between 5 and 11 minutes and temperature values between 37 and 62°C. With the Uvitex NFW/Hercosett system, however, it would be for treatments longer than 8–10 minutes, whatever the temperature, though for short times the temperature has to be lower than 70°C and for long times it must be higher than 50°C.

As our results show, we can establish two clear contradictory tendencies: the Blankophor/Hercosett system promotes improved shrinkproofing at low times and temperatures, whereas Uvitex NFW/Hercosett and Uvitex CF-200/Hercosett promote better shrinkproofing at higher times and temperatures (Figure 3). These results may be explained by considering the physicochemical stability of all these systems with regard to the oxidative action of the hydrogen peroxide reagent in the range of temperatures and times studied, and the influence of these parameters in attracting and fixing the dispersed systems on wool.

Ball Penetration Resistance Loss

Ball penetration resistance loss (BPR%) of samples treated with OBA/Hercosett systems increases with time and temperature (Figure 4) in a way similar to cysteic acid content (Figure 6) and alkaline solubility (Figure 7), that is, 10% of the maximum value accepted in the test [13].

For the Blankophor/Hercosett system, we obtained values of BPR higher than 10% in the range of times and temperatures where there was any shrinkproofing effect. With both Uvitex/Hercosett systems, we obtained unacceptable BPR% values higher than 10% with treatments longer than 15 minutes and higher than 65°C.

Whiteness Degree

Figure 5 shows the whiteness level or index (%), which is the 100% level of the degree of whiteness obtained for samples treated with OBA using treatment conditions recommended by the manufacturer. Referring to the whiteness index values, we obtained a similar improvement for each dispersion system as a function of time and temperature. This effect could be imputed to both the logical exhaustion on wool of the free OBA molecules in equilibrium with those complexed with the Hercosett resin and the bleaching effect due to the oxidative action of the hydrogen peroxide during the treatments (Figure 5). As Figure 5 shows, time has less influence on whiteness than temperature. With temperatures higher than 70°C, a whiteness index greater than 100% can be obtained.

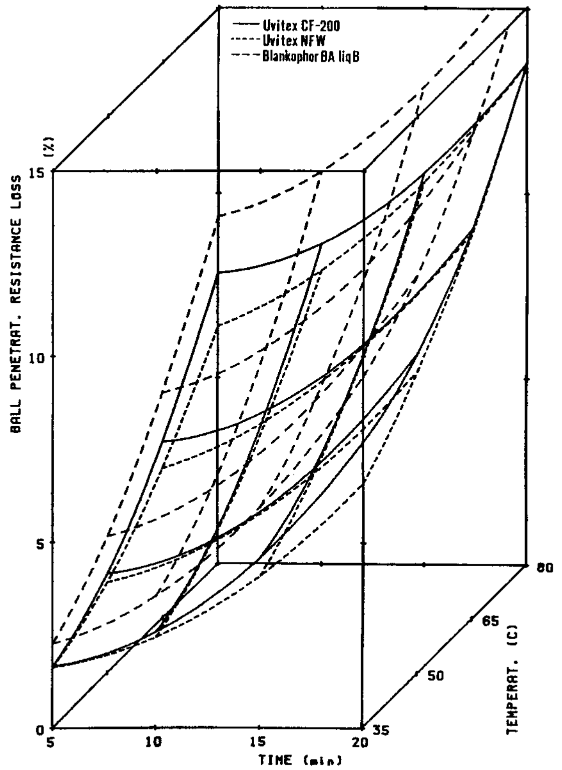

FIGURE 4. Spatial response surfaces of ball penetration resistance loss of treated wool fabrics with different OBA/Hercosett/H_2O_2 complexes versus time and temperature.

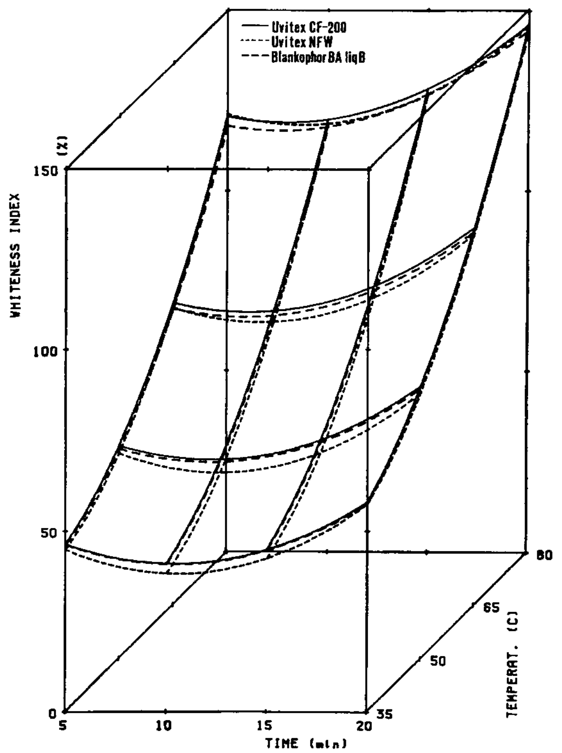

FIGURE 5. Spatial response surfaces of whiteness index of treated wool fabrics with different OBA/Hercosett/H_2O_2 complexes versus time and temperature.

CHEMICAL PARAMETERS

In order to detect the chemical degradative effect of the presence of hydrogen peroxide in the system, in addition to ball penetration resistence loss, we studied the cysteic acid content (Figure 6) and alkaline solubility (Figure 7) of the treated wool samples. Both increase linearly with time and temperature, and both show an acceptable level of fiber chemical modification. In no case did the cysteic acid content exceed 1.5% nor the alkaline solubility 28% [16, 20, 21]. Considering these chemical parameters, there is a similar tendency to oxidative damage in all cases, independent of the OBA agent.

Conclusions

From the results reported in this paper, we can conclude that applying Hercosett resin on untreated wool knitted fabrics via Hercosett/anionic optical brightener agent systems including oxidizing reagents like hydrogen peroxide promotes improved shrinkproofing and whiteness properties. Applying these systems within a certain margin of weight relative to the ratio of both resin and OBA components causes minimum deterioration in the keratin structure.

Applying complexes formed by Hercosett resin, hydrogen peroxide, and three different OBAs to untreated wool fibers has been optimized by keeping treatment time and temperature values between 5 and 20 minutes and 35 and 80°C, respectively. Treatments in all cases promoted improved shrinkproofing and whiteness properties. The Hercosett/Blankophor BA Liq. B complex was the most unstable system, improving shrinkage and whiteness of treated samples only at low times and temperatures; both Hercosett/Uvitex systems were more stable, promoting shrinkage and whiteness improvements at higher times and temperatures. The physicochemical damage of treated wool fibers was in all cases directly dependent on both time and temperature, depending only slightly on the OBA used in each system.

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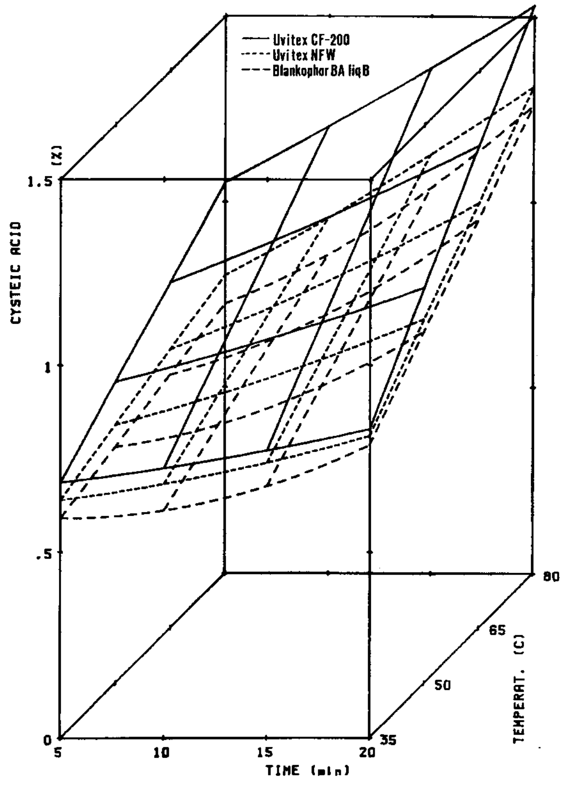

FIGURE 6. Spatial response surfaces of cysteic acid of treated wool fabrics with different OBA/Hercosett/H_2O_2 complexes versus time and temperature.

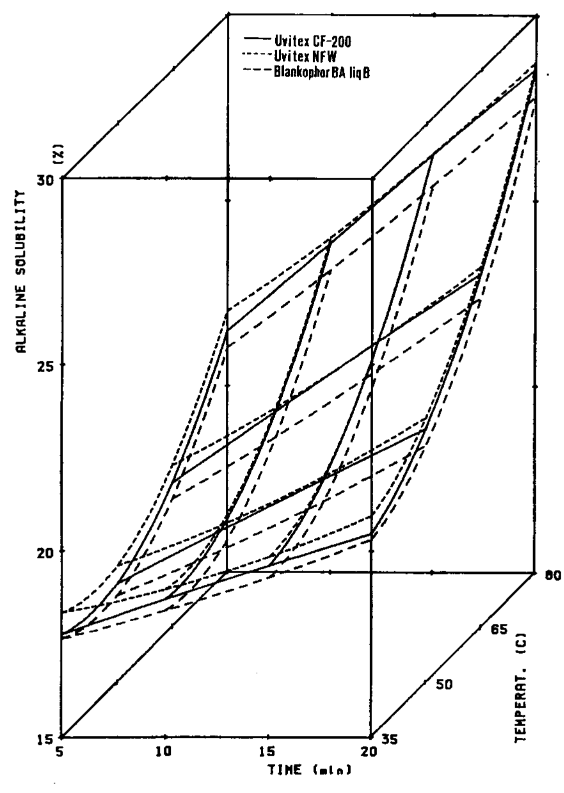

FIGURE 7. Spatial response surfaces of alkalyne solubility of treated wool fabrics with different OBA/Hercosett/H_2O_2 complexes versus time and temperature.

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